

CLAIMS

1. A method for selectively opening rings in polyhedral oligomeric silsesquioxane (POSS) compounds to form functionalized derivatives comprising, reacting  $[(RSiO_{1.5})_n]_{\Sigma \#}$  with an acid to form POSS species bearing one or more functionalities suitable for polymerization, grafting or catalysis, where R is aliphatic, aromatic, olefinic, alkoxy, siloxy or H, n is 4-24, # is n and said acid is  $HBF_4/BF_3$ ,  $CF_3SO_3H$ ,  $ClSO_3H$ ,  $CH_3SO_3H$ ,  $H_2SO_4$ ,  $HClO_4$ ,  $HCl$ ,  $HBr$ ,  $HI$ ,  $HF$  or combinations thereof.
2. The method of claim 1 wherein at least one Si-O-Si bond is shifted in said compound after adding said acid.
3. A method for selectively opening the rings in POSS compounds to form functionalized POSS derivatives comprising, reacting  $[(RSiO_{1.5})_n]_{\Sigma \#}$  with a strong acid to form  $[(RSiO_{1.5})_n(RXSiO_{1.0})_m]_{\Sigma \#}$ , where n is 4-24, m is 1-10, # is m+n, R is aliphatic, aromatic, olefinic, alkoxy , siloxy or H and X is the conjugate base of said acids, which base is F, OH, SH, NHR, NR<sub>2</sub>, ClO<sub>4</sub>, SO<sub>3</sub>CH<sub>3</sub>, SO<sub>3</sub>CF<sub>3</sub>, SO<sub>3</sub>OH, SO<sub>3</sub>Cl, SO<sub>3</sub>CH<sub>3</sub>, NO<sub>3</sub>, PO<sub>4</sub> or Cl.
4. The method of claim 3 wherein organo or organosilicon reagents are added to replace said  $(RXSiO_{1.0})_m$  with functionalities selected from the group of silanes, silylhalides, silanols, silylamines, organohalides, alcohols, alkoxides, amines, cyanates, nitriles, olefins, epoxides, organoacids, esters, vinyl, hydride and strained olefins for grafting, polymerization, or catalysis reactions.
5. The method of claim 3 wherein the POSS compound to be opened is  $[(RSiO_{1.5})_n]_{\Sigma \#}$ ,  $[(RSiO_{1.5})_n(R^3SiO_{1.5})_m]_{\Sigma \#}$  or  $[(RSiO_{1.5})_n(R^1R^2SiO_{1.0})_m]_{\Sigma \#}$ . where n is 6-12, where R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are different substituents selected from the group of aliphatic, aromatic, olefinic, alkoxy, siloxy or H and where # is the sum of the lettered substituents in said POSS compound.
6. The method of claim 3 wherein  $[(RSiO_{1.5})_6]_{\Sigma 6}$  is reacted with said acid to form a compound selected from the group of  $[(RSiO_{1.5})_4(RXSiO_{1.0})_2]_{\Sigma 6}$  and  $[(RSiO_{1.5})_2(RXSiO_{1.0})_4]_{\Sigma 6}$ .

7. The method of claim 3 wherein  $[(RSiO_{1.5})_8]_{\Sigma 8}$  is reacted with said acid to form  $[(RSiO_{1.5})_6(RXSiO_{1.0})_2]_{\Sigma 8}$ .

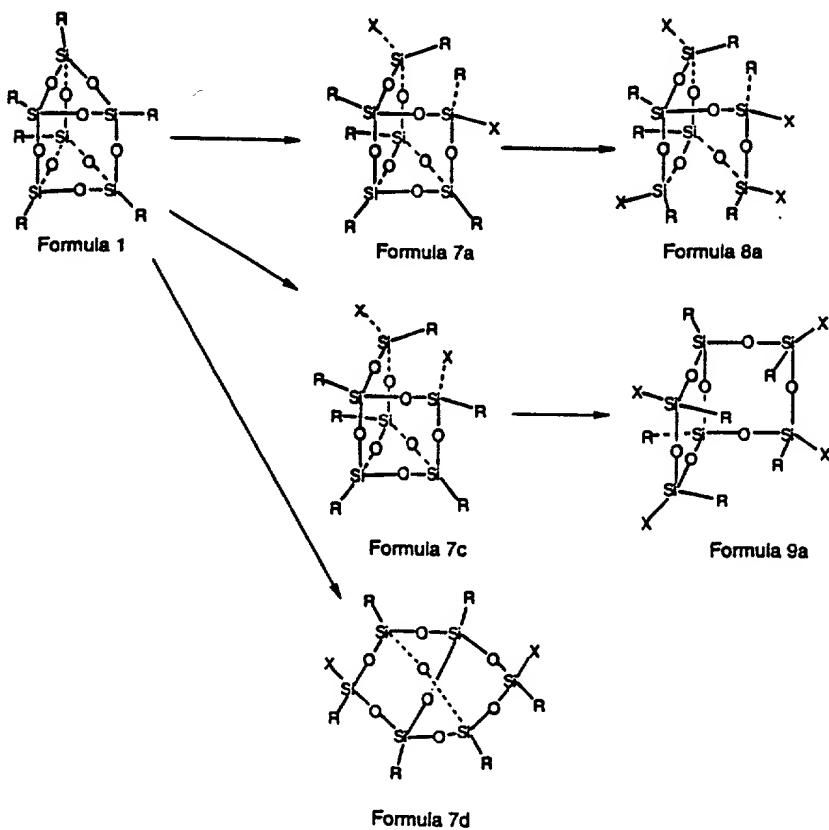
8. The method of claim 3 wherein  $[(RSiO_{1.5})_{10}]_{\Sigma 10}$  is reacted with said acid to form  $[(RSiO_{1.5})_8(RXSiO_{1.0})_2]_{\Sigma 10}$ .

9. The method of claim 3 wherein  $[(RSiO_{1.5})_{12}]_{\Sigma 12}$  is reacted with said acid to form  $[(RSiO_{1.5})_{10}(RXSiO_{1.0})_2]_{\Sigma 12}$ .

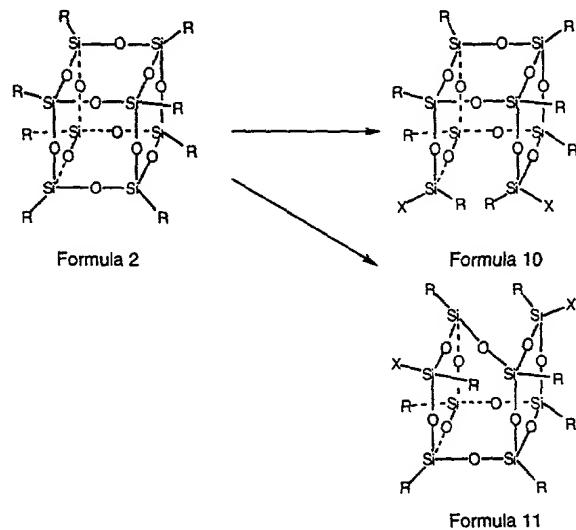
10. The method of claim 3 wherein  $[(RSiO_{1.5})_n(R^3SiO_{1.5})_m]_{\Sigma \#}$  is reacted with said acid to form  $[(RSiO_{1.5})_6(R^3XSiO_{1.0})_1(RXSiO_{1.0})_1]_{\Sigma 8}$ ,  $R^3$  is of the same group as R but is a different substituent and  $\#$  is  $m+n$ .

11. The method of claim 3 wherein  $[(RSiO_{1.5})_7(R^3SiO_{1.5})_1]_{\Sigma 8}$  is reacted with said acid to form  $[(RSiO_{1.5})_4(RXSiO_{1.0})_3]_{\Sigma 7}$  and  $R^3$  is of the same group as R but is a different substituent.

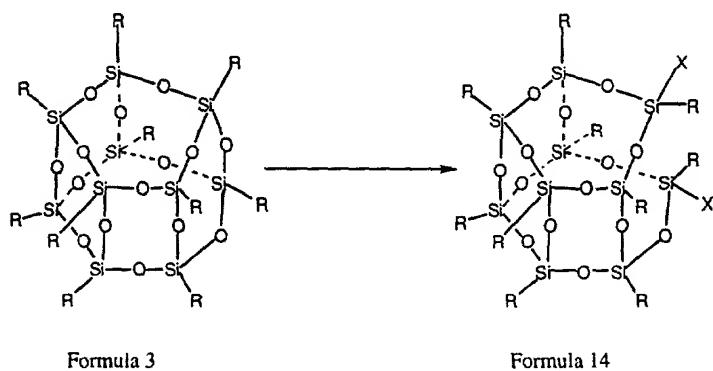
12. The method of claim 3 wherein the compound of formula 1 is reacted with said acid to form a compound of formula 7, 8, or 9 as follows:



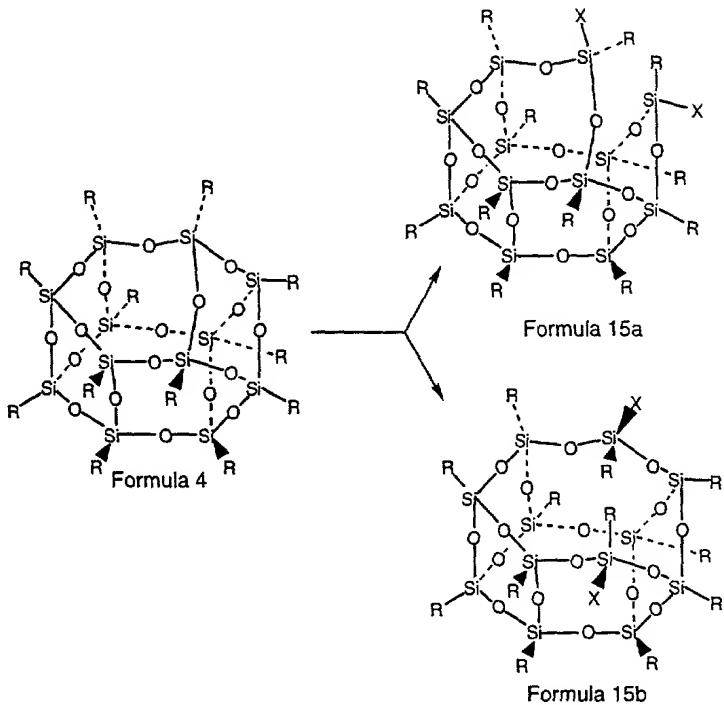
13. The method of claim 3 wherein the compound of formula 2 is reacted with said acid to form a compound of formula 10 or 11 as follows:



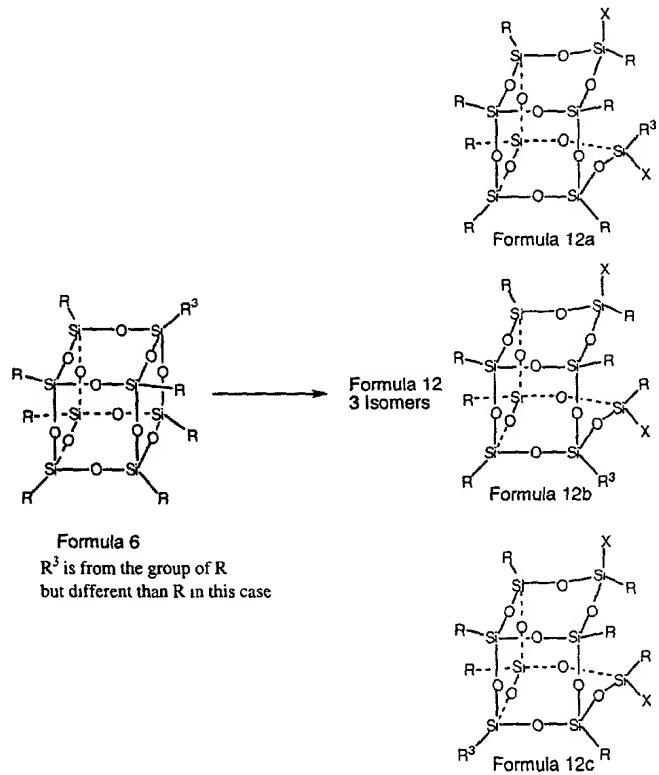
14. The method of claim 3 wherein the compound of formula 3 is reacted with said acid to form the compound of formula 14 as follows:



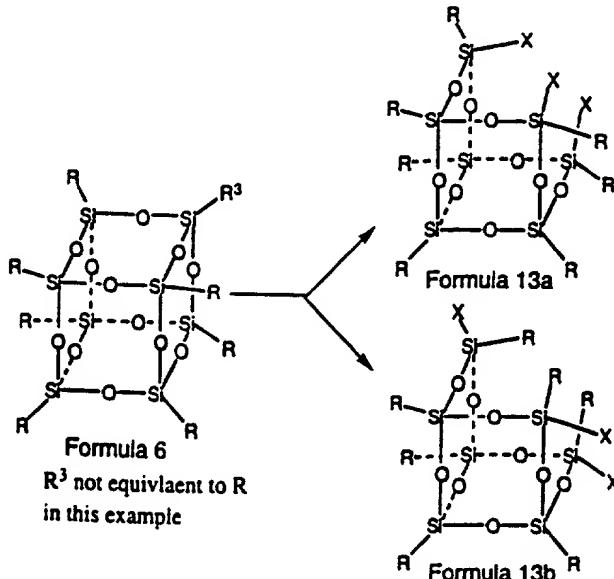
15. The method of claim 3 wherein the compound of formula 4 is reacted with said acid to form a compound selected from the group of formulas 15a and 15b as follows:



16. The method of claim 3 wherein the compound of formula 6 is reacted with said acid to form the compound selected from formulas 12a, b, or c as follows:



17 The method of claim 3 wherein the compound of formula 6 is reacted with said acid to form the compound selected from the group of formulas 13 a and b as follows:



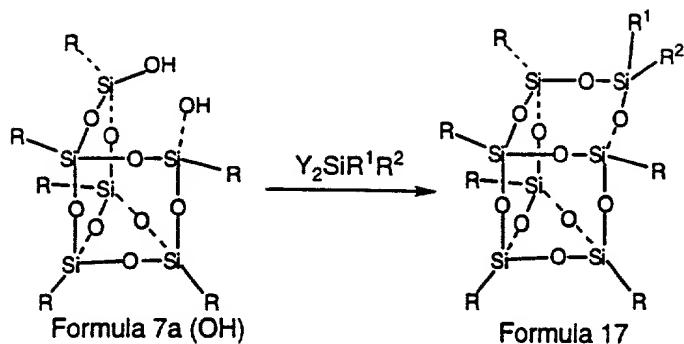
18. A polyhedral oligomeric silsesquioxane (POSS) compound comprising,  $[(RSiO_{1.5})_n(RXSiO_{1.0})_m]_{\Sigma^*}$ , where n is 4-24, m is 1-10, # is m+n, R is aliphatic, aromatic, olefinic, alkoxy, siloxy or H and X is the conjugate base of an acid, which base is of F, OH, SH, NHR or NR<sub>2</sub>, ClO<sub>4</sub>, SO<sub>3</sub>OH, SO<sub>3</sub>CF<sub>3</sub>, SO<sub>3</sub>Cl, SO<sub>3</sub>CH<sub>3</sub>, NO<sub>3</sub>, or PO<sub>4</sub>.

19. The POSS compound of claim 18 selected from the group consisting of all formulas 7-16 above.

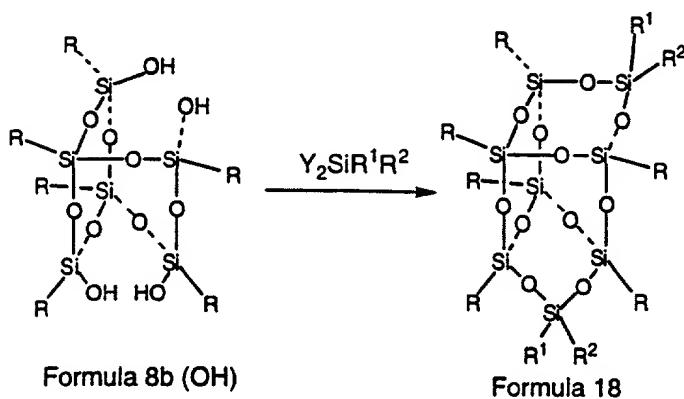
20. A method for expanding rings in polyhedral oligomeric silsesquioxane (POSS) compounds comprising, reacting  $[(RSiO_{1.5})_n(R(HO)SiO_{1.0})_m]_{\Sigma^*}$  with Y<sub>2</sub>SiR<sup>1</sup>R<sup>2</sup> silane reagents to obtain at least one expanded POSS ring in  $[(RSiO_{1.5})_n(R^1R^2SiO_{1.0})_j]_{\Sigma^*}$ , where R, R<sup>1</sup> and R<sup>2</sup> are aliphatic, aromatic, olefinic, alkoxy, siloxy or H, Y is halide or amine, n is 4-24, m is 1-2, j is 1-10 and # is the sum of the lettered substituents in said respective POSS compounds.

21. The method of claim 20 wherein said R, R<sup>1</sup> and R<sup>2</sup> are alkyl, vinyl, allyl or phenyl and Y is a halide selected from the group of Cl, Br, I and F or an amine selected from the group of NH<sub>2</sub> and NR<sub>2</sub>.

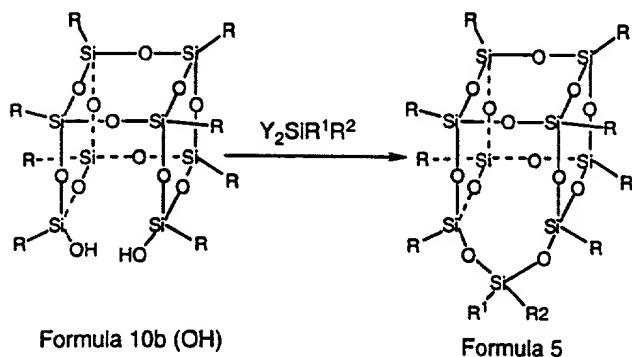
22. The method of claim 20 wherein



23. The method of claim 20 wherein



24 The method of claim 20 wherein



25 A composition having at least one expanded ring in polyhedral oligomeric silsesquioxane (POSS) of the formula  $[(RSiO_{1.5})_n(R^1R^2SiO_{1.0})]_{\Sigma}^*$ , where R,  $R^1$  and  $R^2$  are aliphatic, aromatic, olefinic, alkoxy, siloxy or H, n is 4 – 24, j is 1-10 and # is  $n+j$ .

26 The composition of claim 25 selected from the group consisting of formulas 17, 18 & 5 above.